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Division of Synthetic Chemistry
– Structural Organic Chemistry –

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Scope of Research

Fundamental studies are being conducted for the creation of new functional π-systems with novel structures and properties, and for evaluation of their application as organic semi-conducting materials for photovoltaic and electroluminescent devices. The major subjects are: 1) organochemical transformation of fullerenes C_{60} and C_{70} , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; 2) generation of ionic fullerene species and their application for the synthesis of functional material; 3) synthesis of new carbon-rich materials by the use of transition metal complex; and 4) creation of new functional π-materials with unique photoelectric properties.

KEYWORDS

π-Conjugated Systems
Functional Materials
Organic Solar Cells
Endohedral Fullerenes
Perovskite-Based Solar Cells

Selected Publications

Futagoishi, T.; Murata, M.; Wakamiya, A.; Murata, Y., Trapping N_2 and CO_2 on the Sub-Nano Scale in the Confined Internal Spaces of Open-Cage C_{60} Derivatives: Isolation and Structural Characterization of the Host–Guest Complexes, *Angew. Chem. Int. Ed.*, **54,** 14791-14794 (2015).

Nishimura, H.; Eliseeva, M. N.; Wakamiya, A.; Scott, L. T., 1,3,5,7-Tetra(Bpin)azulene by Exhaustive Direct Borylation of Azulene and 5,7-Di(Bpin)azulene by Selective Subsequent Deborylation, *Synlett*, **26,** 1578-1580 (2015).

Wakamiya, A.; Yamaguchi, S., Designs of Functional π-Electron Materials based on the Characteristic Features of Boron, *Bull. Chem. Soc. Jpn.*, **88,** 1357-1377 (2015).

Wang, S.; Yang, D.-T.; Lu, J.; Shimogawa, H.; Gong, S.; Wang, X.; Mellerup, S. K.; Wakamiya, A.; Chang, Y.-L.; Yang, C.; Lu, Z.-H., In Situ Solid-State Generation of $(BN)_2$-Pyrenes and Electroluminescent Devices, *Angew. Chem. Int. Ed.*, **54,** 15074-15078 (2015).

Chaolumen; Murata, M.; Sugano, Y.; Wakamiya, A.; Murata, Y., Electron Deficient Tetrabenzo-Fused Pyracylene and Conversions into Curved and Planar π-Systems with Distinct Emission Behaviors, *Angew. Chem. Int. Ed.*, **54,** 9308-9312 (2015).

Trapping N_2 and CO_2 on the Sub-nano Scale in the Confined Internal Spaces of Open-cage C_{60} Derivatives: Isolation and Structural Characterization of the Host–Guest Complexes

We have previously reported the synthesis of open-cage C_{60} **1** with a 17-membered-ring opening and one sulfur atom on the rim. It was found that **1** was able to encapsulate molecular nitrogen and carbon dioxide after its exposure to high pressures of N_2 and CO_2 gas. A subsequent reduction of one of the four carbonyl groups on the rim of the opening induced a contraction of the opening (→**2**) and trapped the guest molecules inside. The molecular structures of N_2@**2** and CO_2@**2** were determined by single-crystal X-ray diffraction analyses, which revealed a short N≡N triple bond for the encapsulated N_2 and an non-symmetric molecular structure for the encapsulated molecule of CO_2.

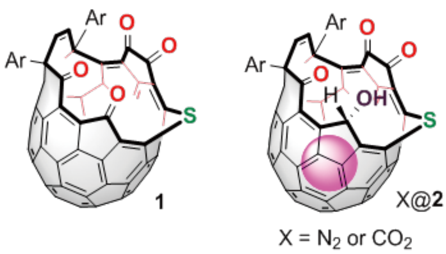

Figure 1. The structures of open-cage C_{60} derivative **1** and host–guest complexes N_2@**2** and CO_2@**2**.

Hole-transporting Materials with a Two-dimensionally Expanded π-System around an Azulene Core for Efficient Perovskite Solar Cells

Two-dimensionally expanded π-systems, consisting of partially oxygen-bridged triarylamine skeletons that are connected to an azulene (**1**–**3**) or biphenyl core (**4**), were synthesized. When tetra-substituted azulene **1** was used as a hole-transporting material (HTM) in perovskite solar cells, the observed performance (power conversion efficiency = 16.5%) was found to be superior to that of the current HTM standard Spiro-OMeTAD. Based on a comparison of the optoelectronic and electrochemical properties of **1**–**4** and Spiro-OMeTAD, we were able to elucidate the factors that are required for HTMs to act efficiently in perovskite solar cells.

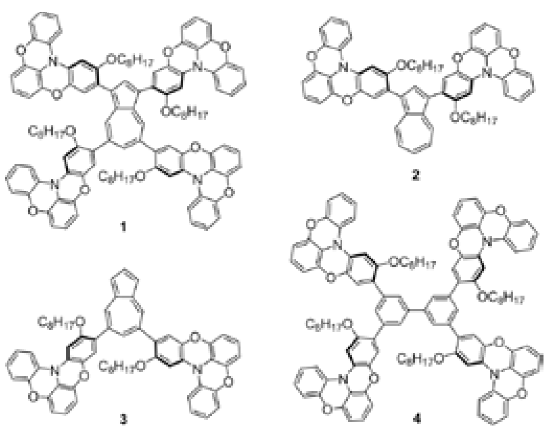

Figure 2. The structures of **1**–**4** with two-dimensionally expanded π-systems.

Electron Deficient Tetrabenzo-fused Pyracylene and Conversions into Curved and Planar π-Systems with Distinct Emission Behaviors

Polycyclic aromatic compounds containing fully unsaturated five-membered ring(s) have been intensively studied because of their unique properties, which include high electron affinity and reactivity. We demonstrated an efficient route for the synthesis of electron-deficient tetrabenzo-fused pyracylene **1** by using intramolecular oxidative C–H coupling. Compound 1 was shown to possess high electron affinity and to undergo addition reactions with *n*-butyllithium or benzyne. These reactions led to either a 1,4-addition compound **2** or triptycene-type adduct **3** with a curved or planar π-system, respectively. These compounds showed distinct emissions in the solid state with high quantum yields. X-ray diffraction analyses demonstrated that the **2** forms dimers with effective π-overlap, which can cause a significant red-shift in the fluorescence by the stabilization of excimer.

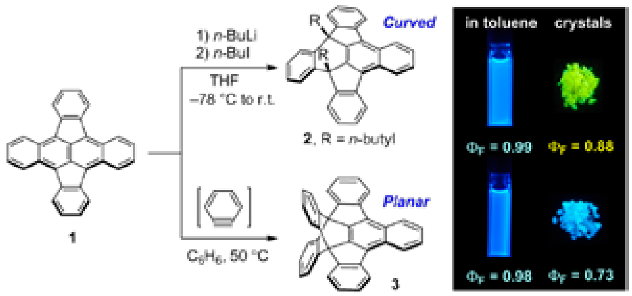

Figure 3. Conversions of electron deficient TBP **1** into curved and planar π-systems **2** and **3** having distinct emission behaviors.